

Quantum Molecular Dynamics Simulations of Nanotube Tip Assisted Reactions

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Abstract

In this report we detail the development and application of an efficient quantum molecular dynamics computational algorithm and its application to the nanotube-tip assisted reactions on silicon and diamond surfaces. The calculations shed interesting insights into the microscopic picture of tip surface interactions.

Final
SCIENTIFIC REPORT FOR
NAG 2-1208

Mad

MAR 06 2000

CC: 202A-36

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The nanotube-tip assisted reactions on silicon and diamond surfaces that are studied at NASA AMES are a precursor to studying microscopic possibilities of mechano-synthesis of materials on solid surfaces. It is shown that using a chemically modified nanotube tip [1] it is possible to selectively deposit few carbon atoms on a diamond surface and selectively etch silicon atoms from a silicon surface. Requiring large scale simulations of reaction trajectories which are run many times with varying initial conditions, these studies have utilized molecular dynamics code with atomic interactions defined by classical many-body potentials. [2] The code is implemented on NAS's parallel machines suitable for large scale molecular dynamics simulations with hundred thousands of atoms. [3]

The classical potentials, however, are inadequate for the very accurate modeling of the microscopic details and structural properties of the tip-surface interaction region. This is because the interactions are local and highly directional, requiring a detailed quantum mechanical treatment. Also, classical potentials cannot provide the electronic structure of the system, crucial in determining many of the relevant properties.

With this in view, we took a two step approach. In the first, we performed large scale computer simulations employing classical potential to determine suitable sets of tip-surface interaction regions leading to carbon nanotube tip assisted mechano-chemical reactions. In the next step, we chose a relatively small "subspace" region consisting of several hundreds of atoms, while containing parts of the tip and the surface, and performed quantum molecular dynamics simulations for this subspace keeping the remaining regions fixed. The fully relaxed subspace provides a detailed microscopic picture of actual tip-surface interactions.

The quantum mechanical simulations were performed using a nonorthogonal tight-binding Hamiltonian [4-6] developed by the PI Menon. The molecular dynamics method based on nonorthogonal tight-binding scheme allows for full relaxation of the systems with no symmetry constraints, and has been found to be very reliable in the treatment of carbon and silicon systems. Since the present project involved interactions of mixed systems containing Si, C and H atoms, the present scheme was extended to model these interactions. The distance dependence of the parameters in the model is a simple exponential

form and this form is taken to be the same for all species. This feature allows us to vary only the input data while treating different elements. Furthermore, due to the efficient way of surface modeling the interactions, only four adjustable parameters were needed for each element. The extension of the method to treat hetero-atomic interactions involved no additional parameters.

I. RESULTS

Silicon and diamond surfaces were modeled using clusters consisting of several thousands of atoms. Furthermore, the nanotube consisted of several hundreds of atoms. In order for a realistic simulations of tip surface interactions, various connectivities between the tip and the surface were explored. They included connectivity via a benzene ring as well as through a linear chain of carbon atoms. All the structures were first relaxed using Brenner's classical three-body potential. [2] A small "subspace" consisting of several hundreds of atoms was selected in each of these cases and quantum molecular dynamics was then performed for this "subspace". Surprisingly, in most of these cases the positions of atoms in the subspace did not change in any substantial manner, save for some symmetry lowering distortions due to the electronic rearrangement. This indicated that the classical three body potential [2] can be relied on for structural determinations when such structures consists of diamond surfaces, carbon nanotubes and benzene rings. The most striking discrepancy was obtained when the connectivity between the nanotube and the surface was through a linear chain of carbon atoms. In the quantum mechanical simulations the chain was broken, disconnecting the tip from the surface. The differences in the geometries are illustrated in Figs. 1 and 2. In Fig. 1 we show the relaxed structure obtained using the three-body potential. The relaxed structure obtained using quantum molecular dynamics is shown in Fig. 2.

Simulations were repeated with a silicon surface. Although, classical potential based simulations showed the tip to surface connectivity through a linear chain of Si atoms to be stable (Fig. 3), qualitatively different results were obtained for the quantum simulations,

where again, the chain was broken (Fig. 4).

Our results, thus, conclusively demonstrate the fact that, while classical potentials have their place in atomistic simulations, the structural predictions obtained using them can be qualitatively incorrect. Quantum simulations, on the other hand, require enormous computational resources for the treatment of large systems. The approach presented in the present work, namely a combination of both methods, thus, offers the best compromise for large scale simulations with detailed structural information in a small region.

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FIGURES

FIG. 1. The relaxed structure for the nanotube tip interacting with the diamond surface via a linear chain of carbon atoms, obtained using a classical three-body potential.

FIG. 2. The relaxed structure for the nanotube tip interacting with the diamond surface via a linear chain of carbon atoms, obtained using quantum mechanical simulations.

FIG. 3. The relaxed structure for the nanotube tip interacting with the silicon surface via a linear chain of Si atoms, obtained using a classical three-body potential.

FIG. 4. The relaxed structure for the nanotube tip interacting with the silicon surface via a linear chain of Si atoms, obtained using quantum mechanical simulations.

Fig. 1

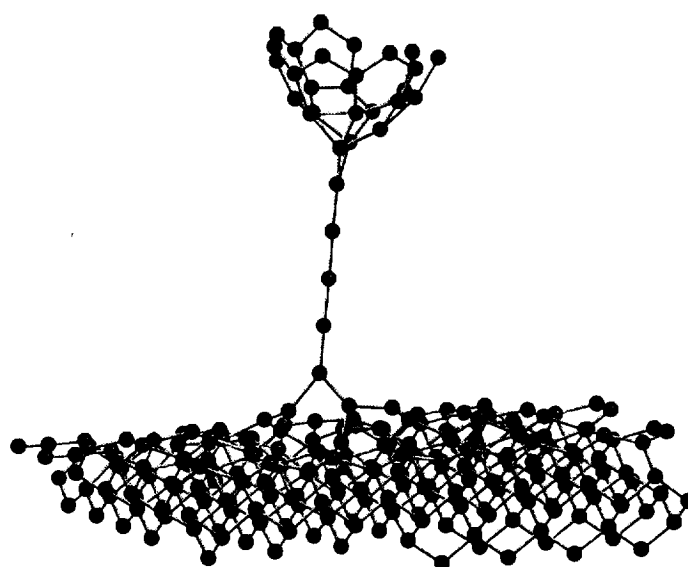


FIG. 2

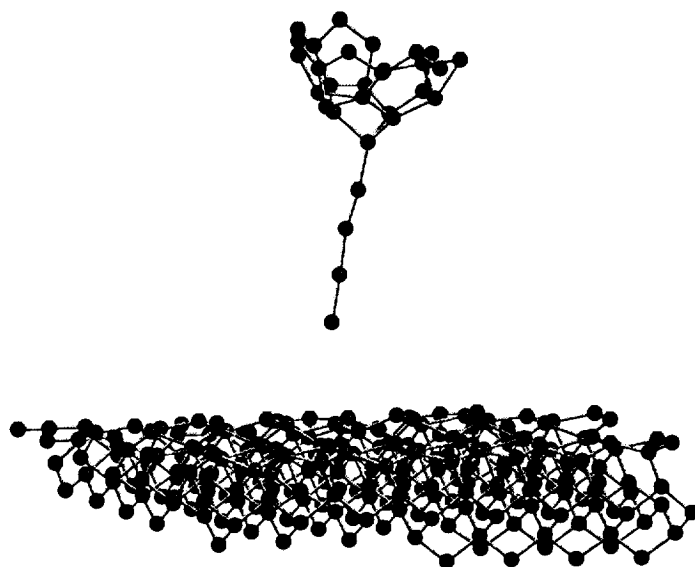


Fig. 3

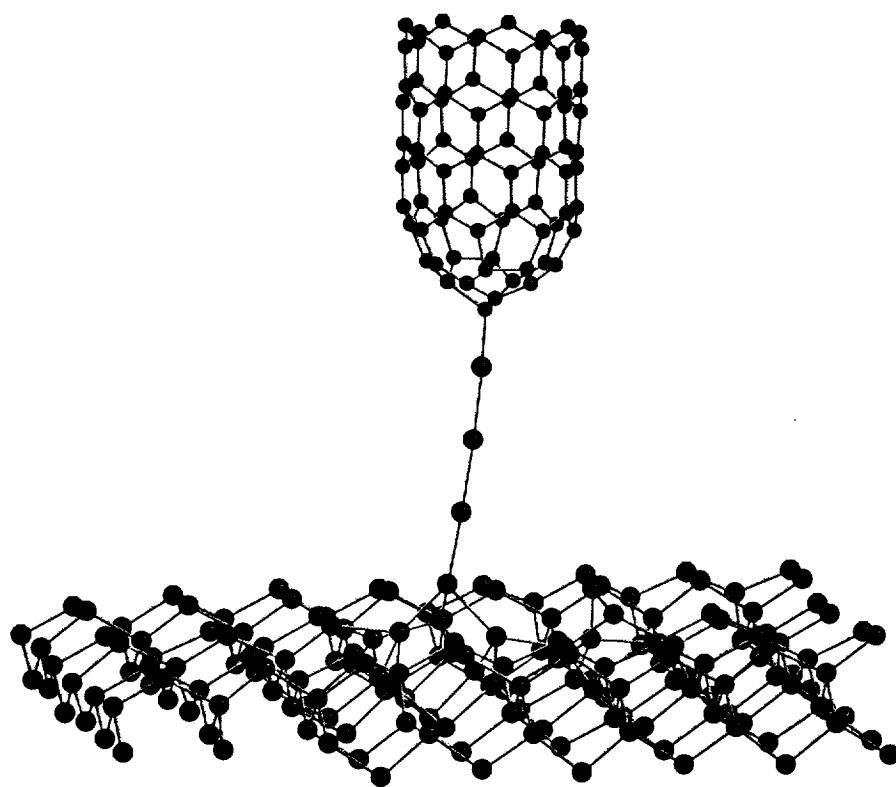


Fig-4

